

Ex-situ Processing of High- J_c Thick YBCO Films on Flexible Metallic Substrates

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Abstract—We present an experimental study of the growth mechanism and superconducting properties of 1 – 5 μm thick YBCO layers on flexible metallic substrates for coated conductor applications. We analyze factors influencing the growth kinetics and nucleation of thick ex-situ processed films. Two processes are assumed to be of major importance for stable growth of c -axis oriented thick films: diffusion of water vapor down to the growth front and of hydrofluoric acid to the film surface. A simple model of the film growth is proposed, suggesting possible ways of improving thick films J_c . Using a modified growth technique we have obtained good superconducting properties for 1 and 3 μm thick YBCO layers on RABiTS tapes, $T_c = 91$ K, $J_c \approx 10^5$ A/cm² at 1 T (77 K, H||c) and $I_c = 45$ A (77 K, 0 T) for a 3 μm thick layer on a RABiTS tape. The transport properties of thick film samples are analyzed along with TEM and X-ray data to establish a correlation between J_c and the structural features of the YBCO layer and substrate-YBCO interface.

I. INTRODUCTION

Ex-situ processing techniques are possible candidates for large-scale production of YBCO coated conductors. The variation of the *ex-situ* method used by us involves two steps: (i) vacuum deposition of Y, Cu and BaF₂ onto an unheated substrate (ii) subsequent heat treatment during which epitaxial growth of YBCO takes place. It has been shown that the method is capable of producing c -axis oriented YBCO layers up to 5 μm thick on SrTiO₃ single crystals [1, 2] and 0.3 μm thick layers on RABiTS tapes [3]. Critical current densities of 2×10^5 A/cm² at 1 T (H||c) were routinely obtained for 1 – 5 μm thick layers on SrTiO₃ and over 10^6 A/cm² on 0.3 μm thick layers on RABiTS tapes in self field.

While naturally occurring defects in YBCO are capable of providing high J_c values, weak links such as high angle grain boundaries (GB's) can considerably affect the overall critical current. We specify three sources of high-angle GB's: a -axis and randomly nucleated grains, and GB's transferred epitaxially from the substrate. Understanding the nucleation and growth of YBCO during *ex-situ* heat treatment can provide control of the film the nucleation process and film properties.

II. EXPERIMENTAL

The Y and Cu were deposited using electron beam guns

The work at BNLaboratory was performed under the auspices of U. S. Department of Energy, contract No. DE-AC02-98CH10886. The work at ORNL was sponsored by DOE under contract DE-AC05-96OR22464.

and a custom 300 W thermal evaporation source was used to deposit the BaF₂. The deposition rate was 14 nm/s as calculated from the thickness crystalline YBCO films

Post deposition processing was performed in a quartz tube. The processing atmosphere was synthesized by mixing certified gases using electronic mass flow controllers. The total gas flow was fixed at 200 sccm and was humidified by bubbling through a heated water bath.

Substrates were Ni RABiTS [4] tapes with a CeO₂-YSZ-CeO₂ composite buffer layer deposited by PLD. Typical in-plane misalignment of the CeO₂ layer, determined by f-scans, was $9 \pm 2^\circ$. The critical current was inferred from transport I - V curves using a 1 $\mu\text{V}/\text{cm}$ electric field criterion.

III. EX-SITU GROWTH MECHANISM

Ex-situ growth chemistry is based on the interaction of BaF₂ with water vapor present in the processing atmosphere and the subsequent formation of HF and YBCO. Growth begins with the nucleation of YBCO at the substrate-precursor film interface and proceeds towards the surface. There are two limiting growth regimes for consideration:

- (i) kinetically limited, when the growth rate is limited by compound formation,
- (ii) diffusion limited, when supply or evacuation of reaction products limits the growth rate.

If the growth rate were kinetically limited then films with predominately a -axis orientation would be expected to grow faster than c -axis films oriented because a -axis grain growth is 10 times faster than c -axis grain growth. Our results show that the growth rate does not depend on the film orientation ruling out kinetically limited growth. In the framework of the diffusion limited model, we need to consider the mass transfer of oxygen and water from the precursor film surface to the growth interface and the diffusion of hydrofluoric acid in the opposite direction. The growth rate does not depend on the oxygen partial pressure in the processing atmosphere [5], which focuses our analysis on the Precursor-YBCO-H₂O-HF kinetics. We assume the growth interface is in steady state equilibrium and that the growth rate is proportional to the HF concentration at the growth interface. Corresponding partial pressures of HF and H₂O are assumed to be related by $P_{\text{HF}}^{0.5}/P_{\text{H}_2\text{O}} = K$, where P is the partial pressure of a reaction component and K is the equilibrium constant. This yields a square root dependence of the growth rate on the water vapor pressure. Fig. 1 shows experimental data of the growth rate

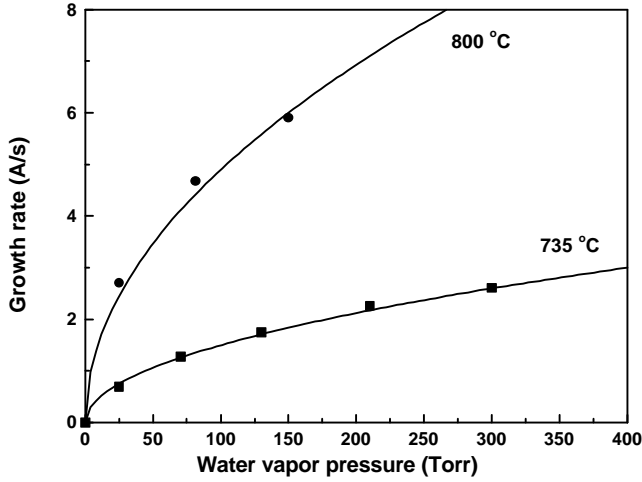


Fig. 1. Growth rate as a function of water vapor partial pressure in the annealing atmosphere for 735 and 800 °C annealing temperature. Solid lines represent square-root approximations.

versus water vapor pressure for 3 – 5 μm films on SrTiO_3 . The solid lines represent the square-root approximation. The good agreement between the data and the model is consistent with the assumption that *ex-situ* YBCO growth is controlled by HF diffusion from the growth interface. An important implication is the role of HF in the nucleation process. HF could participate in two ways: first, high local HF concentrations shift the chemical equilibria and can damage the substrate during the initial stages of the growth affecting the nucleation of the YBCO film [5].

CeO_2 , a popular buffer layer for Ni tapes, has lower resistance to HF than SrTiO_3 . Although films thinner than 1 μm can be grown on CeO_2 using the same method as for SrTiO_3 , the growth of thicker films is unstable with respect to the nucleation of a-axis oriented YBCO grains. During the initial stages of nucleation of thick (>3 μm) YBCO films a layer of Ba-Ce-O forms as a result of chemical interaction between the CeO_2 buffer and the precursor. TEM micrographs of thick YBCO films on CeO_2 substrates show that this layer prevents proper epitaxy and the YBCO film growth often proceeds as a mixture of randomly oriented grains. Such a film, even though having a high T_c has $J_c < 10^4 \text{ A/cm}^2$. We have utilized a substrate preparation technique, which reduces effect of HF damage to the substrate by providing additional channels for rapid HF diffusion through the precursor. Using this technique we succeeded in producing 5 μm thick *c*-oriented YBCO layers with no observable random or a-axis oriented grains. A typical 5 μm YBCO layer exhibited an in-plane alignment of 8° and out-of plane alignment of 4° , $T_c = 91 - 92 \text{ K}$ ($R = 0$).

IV. CRITICAL CURRENTS

Critical current densities of 1 – 5 μm YBCO layers on RABiTS tapes are shown on Fig. 2. Typical J_c values are $0.7 - 0.8 \times 10^5 \text{ A/cm}^2$ (1 T, $H||c$) for a 5 μm thick layer, with an

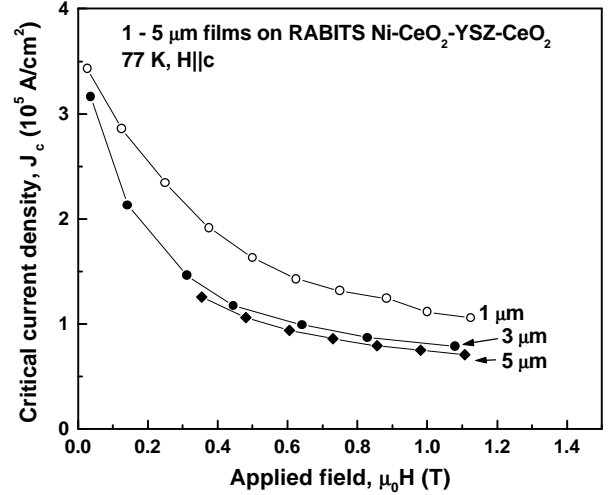


Fig. 2. Transport critical current density versus applied field for 1, 3 and 5 μm films on RABiTS Ni tapes with CeO_2 -YSZ- CeO_2 buffer. Liquid N_2 temperature, external field is parallel to the face of the tape (*c*-axis of the YBCO layer).

extrapolated zero field J_c , between $3 - 4 \times 10^5 \text{ A/cm}^2$. These results are comparable to data from groups using laser ablation for YBCO deposition and similar buffer layer combinations. The critical current density in the YBCO film itself is estimated to be two times higher since the artificially introduced diffusion channels occupy about 50% of the film area. Reduction of substrate area covered by the diffusion channels might improve overall J_c of the films.

Since complete TEM micrographs are not yet available for the coated tapes, we carried out an analysis of microstructure of YBCO thick films on SrTiO_3 annealed at various temperatures and having J_c values changing by a factor of 3. TEM analysis show no correlation between the twin plane density and the J_c value. We did observe a correlation between J_c and the Y_2O_3 precipitate size and density. Thus introduction of reasonable amount of precipitates might further increase the J_c .

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